

## QUANTITATIVE DETERMINATION OF LINESHAPE PARAMETERS FROM VELOCITY MODULATION SPECTROSCOPY

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Velocity Modulation Spectroscopy (VMS) has stood as the gold standard in molecular ion spectroscopy for 30 years. Whether in a traditional uni-directional experiment or more complicated cavity-enhanced layouts with additional layers of modulation, VMS remains the preferred ion detection scheme and is responsible for the detection and transition frequency determination of around 50 molecules.

Despite its success, VMS still has a great deal of untapped potential. There have only been two other published studies<sup>*ab*</sup> of VMS lineshapes and both struggle with the highly correlated parameters: linewidth, intensity, and velocity modulation amplitude, *i.e.* the maximum Doppler shift during a period of the discharge. Due to this difficulty, both Gao and Civiš made concessions to achieve a good fit. Careful analysis of the contour of the transition profile allows us to properly disentangle those parameters in order to probe the environment of the positive column. We can extract the precise values for the translational temperature of the ion, the relative transition intensity, the ion mobility, and the electric field strength just from the lineshape of a single transition. A firm understanding of the lineshape will facilitate chemical and physical investigations of positive columns and allow for a better understanding of more complicated detection schemes.

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<sup>a</sup>H. Gao *et al.*, *Acta Phys. Sin.* **50**, 1463 (2001).

<sup>b</sup>S. Civiš, *Chem. Phys.* **186**, 63 (1994).